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IV.

ON THE ESTIMATION OF PHOSPHORIC ACID AS MAGNESIC PYROPHOSPHATE.

BY F. A. GOOCH.

Presented October 8th, 1879.

THE investigation of which this paper is an account was undertaken at the request of Dr. Wolcott Gibbs, for the purpose of finding, for use in his work upon the complex inorganic acids, the best mode of proceeding in determining the phosphoric oxide of phosphotungstates and phosphomolybdates by precipitation as ammonio-magnesic phosphate and estimation as magnesic pyrophosphate. During the course of the work it has been found necessary to review much of what has been previously published concerning this method of determining phosphoric acid.

In a paper upon this subject, Kubel * criticised Fresenius's correction † (subsequently withdrawn ‡) for the solubility of ammonio-magnesic phosphate in water containing free ammonia and magnesia mixture, and asserted that such correction is not only unnecessary, but that the results of the analysis are of themselves much higher than theory indicates unless the precipitate is, after washing, dissolved and reprecipitated. Kubel's method was to add hydrochloric acid and then ammonia, or ammonic chloride, or ammonia, to a measured amount of a solution of sodic phosphate, to precipitate with magnesic sulphate mixture, and after twelve hours to filter off and wash with dilute ammonia containing one part of strong ammonia to three of water. A number of analyses made in this way gave amounts of phosphoric oxide varying from 101.5 to 104.3 per cent. of the real quantity present, — the actual weight being in each case 0.1986 gr. Another set of analyses in which the precipitate was, after washing, dissolved in hydrochloric acid and again thrown down with ammonia,

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* Zeitschrift für Anal. Chem., VIII., 125.

† Anleitung zur Quant. Anal., 5 Aufl., 333.

‡ Ibid., 6 Aufl. 134.

but which were otherwise treated in the same manner as the first, gave figures for phosphoric oxide varying from 99.8 per cent. to 100.5 per cent. of the real amount. When the precipitate was twice dissolved and twice reprecipitated, the amount of phosphoric oxide indicated was 99.8 per cent., and when three times dissolved and reprecipitated, 99.2 per cent. of the real amount. While noting that the precipitate is not absolutely insoluble in ammonia, more especially if it contain ammonic chloride, Kubel concludes, supposing that a basic sulphate or hydrate of magnesium is thrown down with the first precipitate, that this precipitate must be dissolved after washing and again thrown down with ammonia.

Kissel,* by using large amounts of ammonic chloride, washing copiously in order to make the solubility of the precipitate compensate for the inclusion of foreign matter, and taking care to use no great excess of the magnesic sulphate mixture, obtains in one set of experiments from 99.4 to 99.6 per cent., in another from 99.8 to 100 per cent., of the correct amount of phosphoric oxide. Of three filtrates from the precipitated ammonio-magnesic phosphate two gave weak reactions for phosphoric acid with acid ammonic molybdate, and one no reaction. The wash-water tested by the same method gave in every case a plain reaction. Heintz † supports Kubel so far as to say that in presence of any considerable excess of magnesic sulphate mixture the precipitate must be dissolved after incomplete washing. Brunner ‡ points out that the solution must not be precipitated hot by magnesic sulphate mixture on account of the danger of throwing down magnesic hydrate. Schumann § supports Kissel in the view that the solution of the first precipitate is unnecessary, but adds a caution against the addition of ammonia after the magnesic sulphate mixture.

Finally, Abesser, Jani, and Märcker ‖ substantiate Kubel's results, and having proved the presence of a sulphate in the precipitate obtain somewhat better figures by igniting over the blast. Adopting the method of precipitating by magnesic chloride mixture previously suggested by Brassier¶ and Bunsen,** and recommended in the works of Rose* and Fresenius,† their analyses show from 99.96 per cent. to 100.48 per cent. of the true amount of phosphoric oxide. The weight of phosphoric oxide used in each of their experiments was not far from 0.1250 gr. The precipitate was washed until the reaction for chlorine with argentic nitrate failed to appear in the filtrate acidified with nitric acid. The method of precipitating with magnesic chloride and igniting over the Bunsen lamp gave in their hands from 99.96 to 100.48 per cent.; the method of precipitating with magnesic sulphate and igniting over the blast, from 100.4 to 100.7 per cent.; and the method of precipitating with magnesic sulphate and igniting over the Bunsen lamp from 101.4 to 103.1 per cent. of the actual amount of phosphoric oxide.

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* Zeitschrift für Anal. Chem., VIII. 169.

† Ibid., IX. 16.

‡ Ibid., XI. 30.

§ Ibid., XI. 382.

‖ Ibid., XII., 239.

¶ Ann. de Chim. et de Phys. [4] VII. 335.

** Zeitschrift für Anal. Chem. X. 405.

All agree that the precipitated ammonio-magnesic phosphate is soluble to a very considerable extent in dilute ammonia, and to a greater extent in ammonia containing ammonic chloride; that the presence of a magnesia salt tends to prevent the solution of the precipitate; and that when magnesic sulphate is used in excess as a precipitant the precipitate includes, mechanically or otherwise, an appreciable amount of magnesic sulphate, or magnesic hydrate, or both. Kissel and Schumann aim to arrive at correct results by precipitating with as little excess of magnesic sulphate mixture as possible, and compensating for foreign inclusions by dissolving a part of the precipitate. Kubel and Heintz strive to reach the same end by removing the excess of the precipitant, together with the included impurity by filtering off, dissolving, and again throwing down the precipitate.

With this preface I proceed to the description of my own experiments upon this subject.

I have worked with measured portions of solutions of hydro-disodic phosphate, or of microcosmic salt, the standards of which were, in all cases but one, determined by evaporating a known volume to dryness, igniting the residue and weighing the remaining sodic pyrophosphate or metaphosphate as the case might be. In the one exceptional case a known weight of microcosmic salt, freshly crystallized and dried, the volatile constituents of which had been determined by igniting separate portions, was dissolved in a known volume of water. The experiments which fixed the standards of these solutions are given below.

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* Rose's Analytische Chemie, VI. Aufl., 512, bearbeitet von Finkener.

† Anleit. zur Quant. Anal. 6 Aufl. 403.

I.

Two portions of 20 cm^3 each of a solution of hydro-disodic phosphate were evaporated to dryness, and the residue was ignited and weighed as sodic pyrophosphate.

(1) gave of $Na_4P_2O_7$ 0.1217 gr.
(2) „ „ 0.1214 gr.

The solution contained, therefore, 0.1298 gr. of P_2O_5 to every 40 cm^3.

II.

A quantity of microcosmic salt was recrystallized, dried between papers by pressure, and the amount of loss on ignition determined in two portions.

(1) 1.1419 gr. gave of $NaPO_3$ 0.5836 gr. = 51.11%
(2) 0.9846 gr. „ „ 0.5027 gr. = 51.06%

Of this salt 3.7583 gr. were dissolved in water and the solution diluted to one litre. The solution contained, therefore, 0.0512 gr. of P_2O_5 to every 40 cm^3.

III.

The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm^3 0.3490 gr.
(2) „ „ „ „ 0.3490 gr.

Every 40 cm.^{3} contained, therefore, 0.1863 gr. P_2O_5.

IV.

The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.3530 gr.
(2) „ „ „ „ 0.3533 gr.

Every 40 cm.^{3} contained, therefore, 0.1885 gr. P_2O_5.

V.

The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.3512 gr.
(2) „ „ „ „ 0.3514 gr.

Every 40 cm.^{3} contained, therefore, 0.1875 gr. P_2O_5.

VI.

The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.4112 gr.
(2) „ „ „ „ 0.4113 gr.

Every 40 cm.^{3} contained, therefore, 0.2195 gr. P_2O_5.

VII.

The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.3429 gr.
(2) „ „ „ „ 0.3429 gr.

Every 40 cm.^{3} contained, therefore, 0.1831 gr. P_2O_5.

VIII.

The solution contained microcosmic salt.

(1) gave $NaPO_3$ from 40 cm.^{3} 0.3077 gr.
(2) „ „ „ „ 0.3078 gr.

Every 40 cm.^{3}, therefore, contained 0.2142 P_2O_5.

IX.

The solution contained microcosmic salt.

(1) gave $NaPO_3$ from 40 cm.^{3} 0.2897 gr.
(2) „ „ „ „ 0.2900 gr.

Every 40 cm.^{3} contained, therefore, 0.2017 gr. P_2O_5.

X.

The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 20 cm.^{3} 0.0247 gr.
(2) „ „ „ „ 0.0249 gr.

Every 40 cm.^{3} contained, therefore, 0.0265 gr. P_2O_5.

XI.

The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 20 cm.^{3} 0.0249 gr.
(2) „ „ „ „ 0.0250 gr.

Every 40 cm.^{3} contained, therefore, 0.0266 gr. P_2O_5.

XII.

The solution consisted of 71.5 cm.^{3} of Solution IV. diluted to 500 cm.^{3} Every 40 cm.^{3} contained, therefore, 0.0270 gr. P_2O_5.

XIII.

The solution consisted of 71.5 cm.^{3} of Solution IV. diluted to 500 cm.^{3} Every 40 cm.^{3} contained, therefore, 0.0270 gr. P_2O_5.

XIV.

The solution consisted of 61.3 cm.^{3} of Solution VI. diluted to 500 cm.^{3} Every 40 cm.^{3} contained, therefore, 0.0269 gr. P_2O_5.

XV.

The solution consisted of 61.3 cm.^{3} of Solution VI. diluted to 500 cm.^{3}. Every 40 cm.^{3} contained, therefore, 0.0269 gr. P_2O_5.

XVI.

The solution consisted of 125.6 cm.^{3} of Solution VIII. diluted to one litre. Every 40 cm.^{3} contained, therefore, 0.0269 gr. P_2O_5.

Each of the following experiments was made with 40 cm.^{3} of one or another of these solutions diluted (if necessary), so that the volume after precipitation should for the weaker solutions be about 100 cm.^{3}, and for the stronger solutions from 125 cm.^{3} to 150 cm.^{3}.

Precipitation was effected in cold solutions unless the contrary is stated, and, when not otherwise specified, either by a magnesic sulphate mixture consisting of one part of crystallized magnesic sulphate, two of ammonic chloride, four of concentrated ammonia, and eight of water; or by a magnesic chloride mixture containing three parts of crystallized magnesic chloride, eight of ammonic chloride, sixteen of concentrated ammonia, and thirty-two of water. The precipitate of ammonio-magnesic phosphate was, in every case, finally collected on asbestus felt in a perforated platinum crucible according to the process previously described by me,* washed with 60 cm.^{3} to 70 cm.^{3} (applied in successive portions) of a solution of one part of concentrated ammonia to three of water, — this amount being found to be more than sufficient for washing, when the asbestus process is used, until the filtrate ceases to show the presence of chlorine when treated with nitric acid and argentic nitrate, — moistened with a few drops of a solution of ammonic nitrate in ammonia, dried on the vacuum pump, ignited on a platinum crucible-cover, at first gently until fumes of ammonic nitrate no longer appeared, then at a full red heat until the spreading of a glow over the whole residue indicated the formation of the magnesic pyrophosphate.

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* These Proceedings, XIII. 342.

The results of the experiments are tabulated below. The figures of the first column show the weights of magnesic pyrophosphate found, those of the second the corresponding weights of phosphoric oxide, those of the third the weight of phosphoric oxide required by the determinations of the standard of the solution used, those of the fourth the absolute error in the determination of phosphoric oxide, and those of the fifth the percentage error referred to the actual amount of phosphoric oxide present. The Roman numeral standing against the record of each experiment shows which phosphate solution was used in that experiment.

ALKALINE PHOSPHATES.

Experiments (1) to (10) inclusive were made with 40 cm.^{3} each of the phosphate solution. Portions (1) and (2) were precipitated with 20 cm.^{3} of magnesic sulphate mixture. Portions (3) to (6) were treated with 20 cm.^{3} of a magnesic sulphate mixture containing only a small amount of free ammonia, but the same weights of magnesium and ammonium salts as the regular mixture. The first precipitates of (3) and (4) were dissolved in hydrochloric acid and again thrown down by ammonia in presence of the excess of the precipitant, and those of (5) and (6) were dissolved and reprecipitated in this manner twice. Portions (7) to (10) were precipitated with 20 cm.^{3} of magnesic sulphate mixture after being acidulated — (7) and (8) with hydrochloric acid, (9) and (10) with 0.5 gr. of citric acid — and made alkaline with ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent error.
I.	(1)	0.2082 gr.	0.1331 gr.	0.1298 gr.	+0.0033 gr.	+2.54
	(2)	0.2113 gr.	0.1352 gr.	0.1298 gr.	+0.0054 gr.	+4.16
	(3)	0.2104 gr.	0.1346 gr.	0.1298 gr.	+0.0048 gr.	+3.70
	(4)	0.2124 gr.	0.1358 gr.	0.1298 gr.	+0.0060 gr.	+4.62
	(5)	0.2095 gr.	0.1340 gr.	0.1298 gr.	+0.0042 gr.	+3.23
	(6)	0.2097 gr.	0.1342 gr.	0.1298 gr.	+0.0044 gr.	+3.39
X.	(7)	0.0420 gr.	0.0269 gr.	0.0265 gr.	+0.0004 gr.	+1.51
	(8)	0.0427 gr.	0.0273 gr.	0.0265 gr.	+0.0008 gr.	+3.02
	(9)	0.0444 gr.	0.0284 gr.	0.0265 gr.	+0.0019 gr.	+7.17
	(10)	0.0448 gr.	0.0286 gr.	0.0265 gr.	+0.0021 gr.	+7.92

Experiments (11) to (16) inclusive were made with portions of 40 cm.^{3} each of Solution II. Portions (11) and (12) were acidulated with hydrochloric acid and, after the addition of ammonia in excess, precipitated with 6 cm.^{3} of magnesic sulphate mixture. Portions (13) and (14) were acidulated with 0.5 gr. of citric acid and, after the addition of ammonia, treated with 6 cm.^{3} of magnesic sulphate mixture; which amount failing (on account of the presence of a citrate) to throw the phosphoric acid down entirely, 6 cm.^{3} more of the same mixture were added to complete the precipitation. Portions (15) and (16) were acidulated with hydrochloric acid and 0.5 gr. of citric acid, ammonia added in excess and precipitation effected with 12 cm.^{3} of magnesic sulphate mixture. The precipitates of (11), (13), and (15) were filtered off, washed and ignited; those of (12), (14), and (16) were filtered off on paper, drained, dissolved (without previous washing) in hydrochloric acid, thrown down again with ammonia, and, the precipitate having settled, filtered off, after the addition of a few centimeters of magnesic sulphate mixture, upon asbestus, washed and ignited. The precipitates were all thrown down the first time from hot solutions.

		$Mg_2P_2O_7$	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
II.	(11)	0.0811 gr.	0.0519 gr.	0.0512 gr.	+0.0007 gr.	+1.37
	(12)	0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(13)	0.0827 gr.	0.0529 gr.	0.0512 gr.	+0.0017 gr.	+3.31
	(14)	0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(15)	0.0827 gr.	0.0529 gr.	0.0512 gr.	+0.0017 gr.	+3.31
	(16)	0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.

Experiments (17) to (20) inclusive were made with portions of 40 cm.^{3} each of Solution III. To each portion were added 6 cm.^{3} of strong hydrochloric acid, 20 cm.^{3} of strong ammonia, and 20 cm.^{3} of magnesic sulphate mixture. The first precipitate was filtered off on paper, drained, dissolved in hydrochloric acid and thrown down again with ammonia. In portions (17) and (18) the second precipitation was effected instantly by adding concentrated ammonia to the acid solution, the precipitate being consequently quite voluminous, and magnesic sulphate mixture was added after settling. In portions (19) and (20) the second precipitation was brought about more gradually by neutralizing with dilute ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
III.	(17)	0.2928 gr.	0.1873 gr.	0.1863 gr.	+0.0010 gr.	+0.54
	(18)	0.2937 gr.	0.1878 gr.	0.1863 gr.	+0.0015 gr.	+0.80
	(19)	0.2923 gr.	0.1869 gr.	0.1863 gr.	+0.0006 gr.	+0.32
	(20)	0.2925 gr.	0.1871 gr.	0.1863 gr.	+0.0008 gr.	+0.43

In experiments (21) to (26) inclusive 40 cm.^{3} of magnesic sulphate mixture from which the ammonia had been removed by boiling were in each case added to 40 cm.^{3} of the phosphate solution; in (21), (22), (23), and (24) directly, in (25) and (26) after acidifying with 5 cm.^{3} of strong hydrochloric acid and then making faintly but distinctly ammoniacal. In every case dilute ammonia was added gradually at first, and 5 cm.^{3} of strong ammonia after, the settling of the precipitate. Portions (21) and (22) were precipitated hot.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
V.	(21)	0.3112 gr.	0.1991 gr.	0.1875 gr.	+0.0116 gr.	+6.18
	(22)	0.3114 gr.	0.1992 gr.	0.1875 gr.	+0.0117 gr.	+6.24
	(23)	0.3028 gr.	0.1936 gr.	0.1875 gr.	+0.0061 gr.	+3.25
	(24)	0.3048 gr.	0.1949 gr.	0.1875 gr.	+0.0074 gr.	+3.94
VIII.	(25)	0.3469 gr.	0.2219 gr.	0.2142 gr.	+0.0077 gr.	+3.59
	(26)	0.3514 gr.	0.2248 gr.	0.2142 gr.	+0.0106 gr.	+4.94

For experiments (27) to (39) inclusive portions of 40 cm.^{3} each of the phosphate solutions were taken. To portions (27) and (28) were added 12 cm.^{3} of magnesic chloride mixture; to (29) and (30) 5 cm.^{3} of strong hydrochloric acid, strong ammonia to neutralization and 10 cm.^{3} beside, and then 12 cm.^{3} of magnesic chloride mixture; to portions (31) to (39) inclusive 5 cm.^{3} of strong hydrochloric acid, 20 cm.^{3} of strong ammonia and 10 cm.^{3} of magnesic chloride mixture, 5 cm.^{3} more of the same being added, except in experiment (31), after the settling of the precipitate.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
VI.	(27)	0.3430 gr.	0.2194 gr.	0.2195 gr.	—0.0001 gr.	—0.04
	(28)	0.3438 gr.	0.2199 gr.	0.2195 gr.	+0.0004 gr.	+0.18
	(29)	0.3425 gr.	0.2191 gr.	0.2195 gr.	—0.0004 gr.	—0.18
	(30)	0.3435 gr.	0.2197 gr.	0.2195 gr.	+0.0002 gr.	+0.09

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
III.	(31)	0.2902 gr.	0.1857 gr.	0.1863 gr.	—0.0006 gr.	—0.32
	(32)	0.2903 gr.	0.1857 gr.	0.1863 gr.	—0.0006 gr.	—0.32
	(33)	0.2908 gr.	0.1860 gr.	0.1863 gr.	—0.0003 gr.	—0.16
	(34)	0.2913 gr.	0.1863 gr.	0.1863 gr.	0.	0.
	(35)	0.2919 gr.	0.1866 gr.	0.1863 gr.	+0.0003 gr.	+0.16
	(36)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+0.0004 gr.	+0.21
	(37)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+0.0004 gr.	+0.21
IV.	(38)	0.2935 gr.	0.1877 gr.	0.1885 gr.	—0.0008 gr.	—0.42
	(39)	0.2941 gr.	0.1880 gr.	0.1885 gr.	—0.0005 gr.	—0.27

In experiments (40) to (43) inclusive 10 cm.^{3} of strong ammonia were added to 40 cm.^{3} of the phosphate solution and then 10 cm.^{3} of magnesic chloride mixture. The precipitates of (42) and (43) were dissolved by adding hydrochloric acid to the supernatant liquid and thrown down again with ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
V.	(40)	0.2946 gr.	0.1884 gr.	0.1875 gr.	+0.0009 gr.	+0.48
	(41)	0.2950 gr.	0.1887 gr.	0.1875 gr.	+0.0012 gr.	+0.64
	(42)	0.2927 gr.	0.1872 gr.	0.1875 gr.	—0.0003 gr.	—0.16
	(43)	0.2936 gr.	0.1878 gr.	0.1875 gr.	+0.0003 gr.	+0.16

In experiments (44) to (47) inclusive 10 cm.^{3} of strong ammonia were added to 40 cm.^{3} of the phosphate solution, and then 25 cm.^{3} of magnesic chloride. The precipitates of (46) and (47) were dissolved by hydrochloric acid added to the supernatant liquid and again thrown down with ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent error.
IV.	(44)	0.2977 gr.	0.1904 gr.	0.1885 gr.	+0.0019 gr.	+1.01
	(45)	0.2986 gr.	0.1910 gr.	0.1885 gr.	+0.0025 gr.	+1.33
	(46)	0.2952 gr.	0.1888 gr.	0.1885 gr.	+0.0003 gr.	+0.16
	(47)	0.2954 gr.	0.1889 gr.	0.1885 gr.	+0.0004 gr.	+0.21

For each of the experiments (48) to (60) inclusive 40 cm.^{3} of the phosphate solution were taken. Portions (48), (49), (50), and (51) were precipitated with 40cm.^{3} of magnesic chloride mixture containing 4 gr. of ammonic chloride more than the usual amount, the precipitate being added to the phosphate in experiments (48) and (49), the phosphate (gradually) to the precipitant in (50) and (51). In experiments (52) and (53) the solution of the phosphate was acidulated with 8 cm.^{3} of hydrochloric acid, made alkaline with ammonia —

about 4 gr. of ammonic chloride being produced in the process — and precipitated with 40 cm.^{3} of magnesic chloride mixture. In experiments (54) to (60) inclusive 40 cm.^{3} of magnesic chloride mixture from which the ammonia had been expelled by boiling were added to the phosphate solution — in experiments (56), (57), (58), (59), and (60) directly, in (54) and (55) after adding enough ammonia to make the solution smell distinctly of it — and ammonia afterward strong in (57), (58), (59), and (60), but dilute at first in (54), (55), and (56) and strong after the settling of the precipitate. Solutions (59) and (60) were precipitated hot.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent error.
VII.	(48)	0.2880 gr.	0.1842 gr.	0.1831 gr.	+0.0011 gr.	+0.60
	(49)	0.2881 gr.	0.1843 gr.	0.1831 gr.	+0.0012 gr.	+0.66
	(50)	0.2886 gr.	0.1846 gr.	0.1831 gr.	+0.0015 gr.	+0.82
	(51)	0.2888 gr.	0.1847 gr.	0.1831 gr.	+0.0016 gr.	+0.87
	(52)	0.2882 gr.	0.1844 gr.	0.1831 gr.	+0.0013 gr.	+0.71
	(53)	0.2882 gr.	0.1844 gr.	0.1831 gr.	+0.0013 gr.	+0.71
	(54)	0.2865 gr.	0.1832 gr.	0.1831 gr.	+0.0001 gr.	+0.05
	(55)	0.2870 gr.	0.1835 gr.	0.1831 gr.	+0.0004 gr.	+0.22
V.	(56)	0.2931 gr.	0.1875 gr.	0.1875 gr.	0.	0.
	(57)	0.2940 gr.	0.1880 gr.	0.1875 gr.	+0.0005 gr.	+0.27
	(58)	0.2950 gr.	0.1887 gr.	0.1875 gr.	+0.0012 gr.	+0.64
	(59)	0.2983 gr.	0.1907 gr.	0.1875 gr.	+0.0032 gr.	+1.70
	(60)	0.3017 gr.	0.1930 gr.	0.1875 gr.	+0.0055 gr.	+2.93

In experiments (61) to (66) inclusive 5 cm.^{3} of strong hydrochloric acid were added to 40 cm.^{3} of the phosphate solution and then ammonia in slight excess. Portions (61), (62), (63), and (64) were precipitated with 20 cm.^{3} of magnesic chloride mixture. To (65) and (66) were added 20 cm.^{3} of magnesic chloride mixture from which the ammonia had been expelled, and afterward ammonia dilute at the first and strong after the precipitate had settled. Solutions (63), (64), (65), and (66) contained previous to precipitating 3 gr. of sodic chloride each.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XVI.	(61)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11
	(62)	0.0427 gr.	0.0273 gr.	0.0269 gr.	+0.0004 gr.	+1.49
	(63)	0.0430 gr.	0.0275 gr.	0.0269 gr.	+0.0006 gr.	+2.23
	(64)	0.0431 gr.	0.0276 gr.	0.0269 gr.	+0.0007 gr.	+2.60
	(65)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11
	(66)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11

PHOSPHOTUNGSTATES.

In each of the following experiments upon the determination of phosphoric oxide in phosphotungstates 1 gr. of crystallized normal sodic tungstate (Na_2WO_4. 2 H_2O) was dissolved and added to 40 cm.^{3} of a phosphate solution, the phosphotungstate produced by the addition of acid in measured amount or until the yellow color of the solution indicated its formation, and ammonia added until the precipitate first formed redissolved.

In experiments (67) to (76) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid until the solution became yellow, ammonia until it gave its odor distinctly to the solution, and then 20 cm.^{3} of magnesic sulphate mixture. Portions (75) to (79) inclusive were treated in a similar manner, excepting that 5 cm.^{3} of strong hydrochloric acid and no citric acid were added to them. The precipitates of (67), (68), (69), and (70) were filtered off on asbestus, washed, and ignited in the manner previously described. The precipitates of (71), (72), (73), and (74) were filtered off on paper, washed with magnesic sulphate mixture, and then with a few centimeters of ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia, a few centimeters of magnesic sulphate mixture being added after the precipitate had settled. The precipitates of (75) to (79) inclusive were filtered off on paper, washed with magnesic sulphate mixture, dissolved in hydrochloric acid and thrown down again with ammonia, a few centimeters of magnesic sulphate being added after the settling of the precipitate. The second precipitates were filtered off on asbestus, washed, and ignited as usual.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
X.	(67)	0.0439 gr.	0.0281 gr.	0.0265 gr.	+0.0016 gr.	+6.04
	(68)	0.0445 gr.	0.0285 gr.	0.0265 gr.	+0.0020 gr.	+7.55
	(69)	0.0448 gr.	0.0286 gr.	0.0265 gr.	+0.0021 gr.	+7.92
	(70)	0.0455 gr.	0.0291 gr.	0.0265 gr.	+0.0026 gr.	+9.81
	(71)	0.0388 gr.	0.0248 gr.	0.0265 gr.	—0.0017 gr.	—6.41
	(72)	0.0390 gr.	0.0249 gr.	0.0265 gr.	—0.0016 gr.	—6.04
	(73)	0.0391 gr.	0.0250 gr.	0.0265 gr.	—0.0015 gr.	—5.66
	(74)	0.0394 gr.	0.0252 gr.	0.0265 gr.	—0.0013 gr.	—4.90
	(75)	0.0421 gr.	0.0269 gr.	0.0265 gr.	+0.0004 gr.	+1.51
	(76)	0.0426 gr.	0.0272 gr.	0.0265 gr.	+0.0007 gr.	+2.64
XIII.	(77)	0.0424 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr.	+0.37
	(78)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+0.0003 gr.	+1.11
	(79)	0.0428 gr.	0.0274 gr.	0.0270 gr.	+0.0004 gr.	+1.48

In experiments (80) to (82) and (85) to (88) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid until the solution became yellow, ammonia in excess and 20 cm.^{3} of magnesic chloride mixture; in experiments (83) and (84), and (89) to (91) inclusive, 5 cm.^{3} of strong hydrochloric acid (with no citric acid), ammonia in excess and 20 cm.^{3} of magnesic chloride mixture. The precipitates of (85) to (91) inclusive were filtered off on paper, washed with magnesic chloride mixture, dissolved in hydrochloric acid and thrown down again with ammonia. The first precipitates of experiments (80) to (84) and the second precipitates of portions (85) to (91) were collected on asbestus, washed, and ignited as usual.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent error.
XI.	(80)	0.0454 gr.	0.0290 gr.	0.0266 gr.	+0.0024 gr.	+ 9.02
	(81)	0.0464 gr.	0.0297 gr.	0.0266 gr.	+0.0031 gr.	+11.65
	(82)	0.0466 gr.	0.0298 gr.	0.0266 gr.	+0.0032 gr.	+12.03
XVI.	(83)	0.0444 gr.	0.0284 gr.	0.0269 gr.	+0.0015 gr.	+ 5.58
	(84)	0.0447 gr.	0.0286 gr.	0.0269 gr.	+0.0017 gr.	+ 6.32
XII.	(85)	0.0405 gr.	0.0256 gr.	0.0270 gr.	—0.0014 gr.	— 5.18
	(86)	0.0414 gr.	0.0265 gr.	0.0270 gr.	—0.0005 gr.	— 1.85
	(87)	0.0414 gr.	0.0265 gr.	0.0270 gr.	—0.0005 gr.	— 1.85
	(88)	0.0416 gr.	0.0266 gr.	0.0270 gr.	—0.0004 gr.	— 1.48
XIII.	(89)	0.0423 gr.	0.0270 gr.	0.0270 gr.	0.	0.
	(90)	0.0424 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr.	+ 0.37
	(91)	0.0430 gr.	0.0275 gr.	0.0270 gr.	+0.0005 gr.	+ 1.85

In experiments (92) to (101) inclusive 5 cm.^{3} of strong hydrochloric acid were added to each portion containing the phosphate and tungstate, ammonia in distinct excess, magnesic chloride mixture — in (92), (93), (94), and (95) 1.5 cm.^{3} and 1.5 cm.^{3} more after the precipitate had settled; in (96) and (97) 2 cm.^{3}; in (98) and (99) 5 cm.^{3}; in (100) and (101) 10 cm.^{3} drop by drop and then 10 cm.^{3} more at once — and finally after the precipitate had settled, ammonia until the solution evolved a strong ammoniacal odor.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XIV.	(92)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+0.0002 gr.	+0.74
	(93)	0.0427 gr.	0.0273 gr.	0.0269 gr.	+0.0004 gr.	+1.49
XV.	(94)	0.0428 gr.	0.0274 gr.	0.0269 gr.	+0.0005 gr.	+1.86
	(95)	0.0429 gr.	0.0274 gr.	0.0269 gr.	+0.0005 gr.	+1.86

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XIV.	(96)	0.0430 gr.	0.0275 gr.	0.0269 gr.	+0.0006 gr.	+2.23
	(97)	0.0431 gr.	0.0276 gr.	0.0269 gr.	+0.0007 gr.	+2.60
	(98)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+0.0010 gr.	+3.72
	(99)	0.0440 gr.	0.0281 gr.	0.0269 gr.	+0.0012 gr.	+4.46
XV.	(100)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+0.0013 gr.	+4.83
	(101)	0.0447 gr.	0.0286 gr.	0.0269 gr.	+0.0017 gr.	+6.32

In experiments (102) to (115) inclusive, 5 cm.^{3} of strong hydrochloric acid were added to each portion of phosphate and tungstate, and to portions (112), (113), (114), and (115) 0.5 gr. of citric acid; to every portion, excepting (108) and (109), ammonia in distinct excess; to (108) and (109) ammonia until the precipitate which formed at first was redissolved but not until the solution smelled of ammonia; to all, individually, 20 cm.^{3} of magnesic chloride mixture from which the ammonia had been expelled, and, after the settling of the precipitate, ammonia in strong excess.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XV.	(102)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+0.0010 gr.	+3.72
	(103)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+0.0013 gr.	+4.83
XVI.	(104)	0.0446 gr.	0.0285 gr.	0.0269 gr.	+0.0016 gr.	+5.95
	(105)	0.0454 gr.	0.0290 gr.	0.0269 gr.	+0.0021 gr.	+7.80
	(106)	0.0459 gr.	0.0294 gr.	0.0269 gr.	+0.0025 gr.	+9.29
	(107)	0.0465 gr.	0.0297 gr.	0.0269 gr.	+0.0025 gr.	+9.29
XV.	(108)	0.0498 gr.	0.0318 gr.	0.0269 gr.	+0.0049 gr.	+18.21
	(109)	0.0543 gr.	0.0347 gr.	0.0269 gr.	+0.0078 gr.	+28.99
IX.	(110)	0.3251 gr.	0.2079 gr.	0.2017 gr.	+0.0062 gr.	+3.04
	(111)	0.3262 gr.	0.2086 gr.	0.2017 gr.	+0.0069 gr.	+3.39
	(112)	0.3381 gr.	0.2178 gr.	0.2017 gr.	+0.0161 gr.	+7.91
	(113)	0.3398 gr.	0.2187 gr.	0.2017 gr.	+0.0170 gr.	+8.35
	(114)	0.3423 gr.	0.2190 gr.	0.2017 gr.	+0.0173 gr.	+8.49
	(115)	0.3429 gr.	0.2193 gr.	0.2017 gr.	+0.0176 gr.	+8.64

PHOSPHOMOLYBDATES.

In each of the following experiments upon the determination of phosphoric oxide in phosphomolybdates, 0.5 gr. of molybdic oxide (MO_3) were dissolved in ammonia and added to 40 cm.^{3} of a phosphate solution, 5 cm.^{3} of strong hydrochloric acid added and ammonia in distinct excess. To portions (116) to (120) inclusive were added 20 cm.^{3} of magnesic chloride mixture, and to portions (121) and (122) 20 cm.^{3} of magnesic sulphate mixture. The first precipitates of (119), (120), (121), and (122) were filtered off on paper, dissolved in hydrochloric acid and thrown down again with ammonia, collected on asbestus (as the first precipitates of the other portions were), washed and ignited as usual. Portions (123) and (124) were precipitated with 1.5 cm.^{3} of magnesic chloride mixture, 1.5 cm.^{3} being added after the precipitate had settled, together with ammonia in strong excess. Portions (125) to (129) inclusive were precipitated with 20 cm.^{3} of magnesic chloride mixture from which the ammonia had been expelled, and ammonia was added in strong excess after the settling of the precipitate.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XII.	(116)	0.0441 gr.	0.0282 gr.	0.0270 gr.	+0.0012 gr.	+4.44
	(117)	0.0452 gr.	0.0289 gr.	0.0270 gr.	+0.0019 gr.	+7.04
	(118)	0.0458 gr.	0.0293 gr.	0.0270 gr.	+0.0023 gr.	+8.52
XIII.	(119)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr.	+0.37
	(120)	0.0425 gr.	0.0272 gr.	0.0270 gr.	+0.0002 gr.	+0.74
	(121)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr.	+0.37
	(122)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+0.0003 gr.	+1.11
XVI.	(123)	0.0423 gr.	0.0270 gr.	0.0269 gr.	+0.0001 gr.	+0.37
	(124)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+0.0002 gr.	+0.74
	(125)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+0.0002 gr.	+0.74
	(126)	0.0425 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11
IX.	(127)	0.3168 gr.	0.2026 gr.	0.2017 gr.	+0.0009 gr.	+0.44
	(128)	0.3173 gr.	0.2030 gr.	0.2017 gr.	+0.0013 gr.	+0.64
	(129)	0.3180 gr.	0.2033 gr.	0.2015 gr.	+0.0016 gr.	+0.79

Experiments (1) to (10) inclusive, (11), (13), and (15) demonstrate that the method of estimating the phosphoric oxide of alkaline phosphates by precipitation with magnesic sulphate mixture and washing until the chlorine reaction vanishes from the filtrate gives results far too high when the amount of the precipitant used is in any considerable excess of the amount theoretically required. Thus, in experiments (1) to (6), in each of which 20 cm.^{3} of magnesic sulphate mixture were used, the amount required by theory being about 5.2 cm.^{3}, the error varies from +0.0033 gr. to +0.0060 gr. on 0.1298 gr. of phosphoric oxide, or from +2.54 to +3.39 per cent.; in experiments (7) to (10), in each of which 20 cm.^{3} of the precipitant were used, while theory requires about 1.1 cm.^{3}, the error upon 0.0265 gr. of phosphoric oxide varies from +0.0004 gr. to +0.0021 gr., or from +1.51 to +7.92 per cent.; in experiment (11) in which 6 cm.^{3} of the precipitant were used, while about 2.1 cm.^{3} were theoretically required, the error is +0.0007 gr. upon 0.0512 gr. of phosphoric oxide, or +1.37 per cent.; and in experiments (13) and (15) in which 12 cm.^{3} of the precipitant were used, while about 2.1 cm.^{3} were theoretically required, the error upon 0.0512 gr. of phosphoric oxide was +0.0017 gr., or +3.31 per cent.

Experiments (21) to (26) inclusive show that when the process was varied so as to precipitate the phosphate solution, either containing no free ammonia or a very small quantity, by a magnesic sulphate mixture from which the ammonia had been expelled, the error of the result varied from +0.0061 gr. to +0.0117 gr. upon 0.1875 gr. of phosphoric oxide, or from +3.25 to +6.24 per cent.; and from +0.0077 gr. to +0.0106 gr. upon 0.2142 gr. of phosphoric oxide, or from +3.59 to +4.94 per cent., — the greatest errors appearing naturally in the experiments made with hot solutions containing no free ammonia, in which cases the hydro-magnesic phosphate first thrown down was partially changed into tri-magnesic phosphate by the action of the heat, and therefore not converted into ammonio-magnesic phosphate upon the subsequent addition of ammonia.

Experiments (12), (14), (16), and (17) to (20) inclusive indicate that tolerably good results may be obtained by draining the first precipitate, dissolving in hydrochloric acid and reprecipitating with ammonia; the first three experiments showing incidentally that the addition of small amounts of citric acid does not prevent precipitation to any very marked degree in presence of a considerable excess — in this case about 10 cm.^{3} to 0.5 gr. of citric acid — of magnesic sulphate mixture. Thus in experiments (12), (14), and (16) the error was 0; and in experiments (17) to (20) the error varied from +0.0006 gr. to +0.0015 gr. on 0.1863 gr. of phosphoric oxide, or from +0.32 to +0.80 per cent., the mean error being about +0.0006 gr., or +0.32 per cent.

It appears from these experiments that the method of precipitating by magnesic sulphate mixture without the solution and second precipitation ought to give an accurate determination of phosphoric acid, providing only that the amount of the precipitant used were just sufficient to complete the precipitation. But this condition renders the process practically useless in ordinary cases; and inasmuch as in

Kissel's method of compensating for enclosed material by excessive washing, the amount of washing must necessarily be proportioned both to the weight of phosphoric acid present and to the excess of the precipitant, — elements which introduce a great deal of uncertainty, — it would appear that if magnesic sulphate mixture is to be the precipitant the method of precipitating twice is the only one which can be relied upon on all occasions to give tolerably correct results.

The results obtained in experiments (27) to (66) by precipitating with magnesic chloride mixture are different as the method of treatment varies. It will be noticed that in experiments otherwise essentially similar the variations in the amount of the precipitant produce differences in the results. Thus, in experiments (27) to (43), in which 10 cm.^{3} or 12 cm.^{3} of the precipitant were used, the error varies from —0.0008 gr. to +0.0012 gr., or from —0.42 to +0.64 per cent., the mean error being nearly 0; while in the experiments (48) to (53) in which 40 cm. ^{3} of the precipitant were used, the error varies from +0.0011 gr. to +0.0016 gr., or from +0.60 to +0.87 per cent., the mean error being about +0.0013 gr., or +0.71 per cent. It will be seen also that while it makes no apparent difference whether the precipitant is added to the phosphate directly, as in (27) and (28), or after treatment with hydrochloric acid, as in (29) to (39), the dissolving of a precipitate, by adding hydrochloric acid to the supernatant liquid, and reprecipitation with ammonia tend to reduce the results below those of experiments in which this has not been done, but which are similar in other respects. This appears very distinctly in a comparison of experiments (40) and (41) with (42) and (43), where the mean error is reduced from about +0.0010 gr. upon 0.1875 gr. of phosphoric oxide, or from +0.56 per cent., to 0; or of experiments (44) and (45) with (46) and (47), where the mean error is reduced from +0.0022 gr. to about +0.0003 gr. upon 0.1885 gr. of phosphoric oxide, or from +1.17 to +0.18 per cent.

It appears, further, from a comparison of experiments (54) to (58) with experiments (48) to (53), that results got by precipitating solutions containing either no free ammonia, as in (56), (57) and (58), or only a small amount, as in (54) and (55), by a magnesic chloride mixture deprived of ammonia are more nearly correct than those got by precipitating under essentially similar conditions with the ammoniacal magnesic chloride mixture as in (48) to (53). Thus, in (48) to (53) the error varies from +0.0011 gr. to +0.0016 gr. upon 0.1831 gr. of phosphoric oxide, or from +0.60 to +0.87 per cent., the mean error being about +0.0013 gr. or +0.71 per cent.; while in (54) to (58) the error varies from 0 to +0.0012 gr. upon 0.1831 gr. or 0.1875 gr. of phosphoric oxide, or from 0 to +0.64 per cent., the mean error being about +0.0004 gr. or +0.22 per cent.; and it is to be remarked that in (54), (55) and (56), in which dilute ammonia was added after the non-ammoniacal magnesic chloride mixture, the mean error — about +0.0002 gr. or +0.10 per cent. — is much smaller than the mean error of (57) and (58) — about +0.0008 gr., or +0.44 per cent. — in which strong ammonia was added after the non-ammoniacal magnesic chloride mixture. The high results of experiments (59) and (60), in which the non-ammoniacal magnesic chloride mixture was added to the hot phosphate solution, are explained by the fact that a part of the hydromagnesic phosphate first formed was decomposed by the heat with the formation of trimagnesic phosphate, and therefore not completely converted into ammonio-magnesic phosphate by the ammonia subsequently added. From experiments (61) to (64) it will be seen that the presence of 3 gr. of sodic chloride in the phosphate solution raises the figures of the analysis materially when precipitation is effected by the ammoniacal magnesic chloride mixture, even with small weights of phosphoric oxide, and that better results are got in (65) and (66) by using the non-ammoniacal mixture.

The use of an excessive quantity, too, of ammonic chloride tends apparently to reduce the error. Thus, in experiments (48) to (53) the mean error was about +0.0013, gr., or +0.71 per cent., while in (44) and (45), in which free ammonia, but no ammonic chloride beyond the amount in the magnesic chloride mixture, was used, the mean error is +0.0022 or +1.17 per cent., although less of the precipitant was used in the latter.

The cause of all these differences in the accuracy of the determination of the phosphoric oxide of alkaline phosphates by precipitation with magnesic chloride mixture seems to lie in the variations of the rapidity with which the ammonio-magnesic phosphate is crystallized from solution. The sudden addition of a large amount of the precipitant, or of an excess of the precipitant to a strongly ammoniacal solution of the phosphate, or of strong ammonia to a solution of the precipitate in acid, tends to hasten the deposition, and so to prevent the complete exclusion of foreign material from the crystalline structure; while in the precipitation of solutions containing large amounts of ammonic chloride, or of weakly ammoniacal solutions, or of solutions of the precipitate in acid, by the gradual addition of ammonia the process of crystallization goes on more slowly and perfectly.

The differences between results got by using a magnesic sulphate mixture and those obtained with a magnesic chloride mixture may be, perhaps, partly explained by the supposition that magnesic sulphate resists exclusion during the crystallization of the ammonio-magnesic phosphate more effectively than magnesic chloride, and partly by the fact that magnesic sulphate enclosed in a precipitate would probably not change materially in composition during an ignition over a Bunsen burner in a crucible standing on platinum foil, while magnesic chloride ignited in presence of aqueous vapor under like circumstances would be converted into magnesic oxide whose molecular weight is but one-third of that of the sulphate. It is difficult, at all events, to conceive how the contamination of the precipitate can be other than mechanical; for the trimagnesic phosphate could only be produced by a reaction between the ammonio-magnesic phosphate and magnesic sulphate, — which is quite improbable, at least in the cold, — and the formation of a magnesic hydrate or basic sulphate would seem to be altogether unlikely under the circumstances.

In the experiments upon the phosphotungstates the mean error of the method involving a single precipitation with magnesic sulphate mixture (experiments 67 to 70) was about +0.0021 gr. upon 0.0265 gr. and with magnesic chloride mixture (experiments 80 to 84) about +0.0024 gr., upon 0.0266 gr. or 0.0269 gr., of phosphoric oxide, or about +8.44 per cent. The mean error of the method of double precipitation upon nearly the same amounts of phosphoric oxide, the precipitant alone being used to wash the first precipitate and no citrate being present, was, with magnesic sulphate mixture (experiments 75 to 79) about +0.0004 gr., or +1.51 per cent., and with magnesic chloride mixture (experiments 89 to 91) +0.0002 gr., or +0.74 per cent.; the mean error when the first precipitate by magnesic sulphate mixture was washed with the precipitant and afterwards with ammonia water (experiments 71 to 74) being about —0.0015 gr., or —5.66 per cent.; and when the first precipitate was thrown down in presence of a citrate by magnesic chloride mixture and washed with the precipitant (experiments 85 to 88), about —0.0007 gr., or —2.59 per cent. When precipitation was effected with 1.5 $cm.^3$ of magnesic chloride mixture, the same being added after precipitation (experiments 92 to 95) the mean error upon 0.0269 gr. of phosphoric oxide was +0.0004 gr. or +1.49 per cent.; when by 2 $cm.^3$ (experiments 96 and 97) about +0.0006 gr., or +2.23 per cent.; when by 5 $cm.^3$ (experiments 98 and 99) +0.0011 gr., or +4.09 per cent.; and when by 10 cm^3 added drop by drop, with 10 $cm.^3$ more subsequent to precipitation (experiments 100 and 101) +0.0015 gr., or +5.58 per cent. The mean error of the determination by precipitating with 20 $cm.^3$ of non-ammoniacal magnesic chloride mixture, in slightly ammoniacal solutions (experiments 102 to 107 and 110 to 115) was about +0.0018 gr. upon 0.0269 gr. of phosphoric oxide, or +6.69 per cent.; about +0.0065 gr. upon 0.2017 gr. of phosphoric oxide, or +3.22 per cent., in solutions containing no citrate, and in solutions containing a citrate +0.0170 gr., or +8.35 per cent. The mean error when 20 $cm.^3$ of non-ammoniacal magnesic chloride mixture was added to the solution of phosphate and tungstate containing no free ammonia (experiments 108 and 109) amounted to about +0.0063 gr. upon 0.0269 gr. of phosphoric oxide, or +23.60 per cent.

The use of citric acid in many of the experiments above, in accordance with a suggestion of Dr. Gibbs, appears to be attended with unfavorable results. Thus in experiments (85) to (88), in which the first precipitates were dissolved and reprecipitated, this appears to have lowered the results below those of (89) to (91); while in experiments (80) to (82) and in experiments (112) to (115), in which the first precipitate was not dissolved, it appears to have raised the results above those of (83) and (84), and (110) and (111) respectively, — facts which are perhaps to be explained by attributing to the citrate both a solvent and contaminating action upon the precipitate.

Of the experiments upon the phosphomolybdates (123) and (124), in which the precipitation was effected by 1.5 $cm.^3$ of magnesic chloride mixture, 1.5 $cm.^3$ of the same being added afterward, show a mean error of less than +0.0002 gr. upon 0.0269 gr. of phosphoric oxide, or +0.55 per cent.; and experiments (116) to (118) in which 20 $cm.^3$ of the same precipitant were employed +0.0018 gr. upon 0.0270 gr. of phosphoric oxide, or +6.66 per cent; experiments (119) to (122), in two of which the precipitation was effected by magnesic sulphate mixture and in two by magnesic chloride mixture, the first precipitate being washed with the precipitant, dissolved in hydrochloric acid and again thrown down, less than +0.0002 gr. upon 0.0270 gr. of phosphoric oxide, or +0.65 per cent. In experiments (125) to (129) in which 20 $cm.^3$ of the magnesic chloride mixture deprived of ammonia were added to slightly ammoniacal solutions, the mean error was less than +0.0003 gr. on 0.0269 gr. of phosphoric oxide, or +0.92 per cent., and less than +0.0013 gr. on 0.2017 gr. of phosphoric oxide, or +0.62 per cent.

It will be noticed that in the experiments with phosphates and phosphomolybdates a large excess of the magnesic chloride mixture was not markedly prejudicial to the accuracy of results when precautions were taken to induce a slow formation of the precipitate, while in the experiments with phosphotungstates the reverse was true. The reason for this exceptionally unfavorable action in the case of the phosphotungstates is probably indicated in the facts that the addition of free ammonia beyond a certain amount to the solution of a phosphotungstate produces turbidity, and that the addition of magnesia mixture to a clear solution of normal sodic tungstate, ammonic chloride and ammonia renders the solution opalescent and occasions the deposition, after some hours, of an almost invisible precipitate; but it is to be noted in this connection that the action of magnesia mixture upon a clear ammoniacal solution of ammonic molybdate and ammonic chloride is similar to its action upon the tungstate solution.

SUMMARY.

It would appear from the preceding account that in determining the phosphoric oxide of alkaline phosphates, free from sulphates or other substances likely to contaminate a precipitate, accuracy is most conveniently and surely attained by adding to the somewhat dilute solution of the phosphate ammonia in slight but quite distinct excess, then an excess of magnesic chloride mixture containing no free ammonia (made by dissolving three parts of crystallized magnesic chloride and eight parts of ammonic chloride in water, adding water containing ammonia until the volume of the solution reaches forty-eight parts, filtering and boiling off the free ammonia), and, after the precipitate has settled, ammonia until the liquid evolves a strong odor of it. In determining the phosphoric oxide of phosphotungstates the best results are to be got by adding to the solution containing free ammonia an excess of either of the magnesia mixtures, washing the precipitate with the precipitant, dissolving in hydrochloric acid, diluting if necessary and reprecipitating with a little dilute ammonia, adding strong ammonia after the precipitate has settled; or, when working with small amounts, by proceeding as in the case of the phosphates, taking special care, however, that the solution is distinctly ammoniacal before precipitating, and that no great excess of the precipitant is used. In the determination of the phosphoric oxide of phosphomolybdates, the method recommended for use in the case of the phosphates serves very well when the amount of phosphoric oxide

does not exceed (let us say) 0.05 gr., but for amounts larger than this the method of double precipitation recommended for the phosphotungstates is more accurate.

As to the time which should be allowed to pass between precipitating and filtering, my experiments support those of Abesser, Jani, and Märcker * in pointing to the conclusion that a precipitate may be filtered with safety as soon as it has completely subsided, or, after ten or fifteen minutes.

The use, for the filtration and ignition of the precipitate, of the method which I have employed in the experiments described above greatly expedites the analysis. Thus, with two perforated crucibles at my disposal, I have completed within four and one-half hours from the measuring out of the first solution seven determinations of the phosphoric oxide of an alkaline phosphate, — the ignition of each precipitate requiring less than five minutes.

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* Zeitschrift für Anal. Chem. XII. 250.